NAVY EXPERIMENTAL DIVING UNIT

TECHNICAL REPORT NO. 1-95

EVALUATION OF DRÄGER CO_2 GAS DETECTOR SYSTEM

Donald J. SCHMITT

JANUARY 1995

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NAVY EXPERIMENTAL DIVING UNIT

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This test series evaluated the DRÄGER Co_2 0.1%/a and CO_2 0.01%/a gas detector tubes using the DRÄGER Accuro and the DRÄGER initial test series, conducted in Navy Experimental Diving Unit's (NEDU) treatment chamber during July 1994, evaluated both pumps at one atmosphere, and the CO_2 0.1%/a tube at the surface and 9.1, 27.4, 45.7 and 50.3 meters of

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seawater (MSW) (30, 90, 150 and 165 feet of seawater (FSW). Six certified sources of CO_2 in nitrogen or helium background were sampled by two divers during each dive.

The second test series was conducted in November/December 1994 coincident with NEDU's Deep Dive '94, a 308.4 MSW (1000 FSW) saturation dive conducted in the Ocean Simulation Facility. This test sampled chamber atmosphere, using both tubes and both pumps, and compared those results with readings from the installed system electronic CO_2 monitor.

The 0.1%/a tubes met DRÄGER's accuracy specifications at one atmosphere, but appeared to have degraded accuracy with increased depth. The 0.01%/a tubes were not tested at one atmosphere, but displayed the same characteristics as the 0.1%/a tubes at depth.

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INTRODUCTION

Upgraded versions of current U.S. Navy recompression chambers have electronic CO_2 monitoring capability. However, should these monitors fail during an operation, a suitable backup monitor is necessary for which Dräger CO_2 gas detector tubes appear well suited. While the Dräger gas detector tubes are designed and calibrated for one atmosphere use, they have been used in hyperbaric chambers though lacking concrete verification of their accuracy under hyperbaric conditions.

The basis of the Dräger CO_2 gas detector tube, as stated in the Dräger Handbook, is the chemical reaction of CO_2 oxidizing hydrazine hydrate in the presence of crystal violet as an oxidation-reduction reaction:

$$CO_2 + N_2H_4 \rightarrow NH_2\text{-}NH\text{-}COOH$$

Typically carbon dioxide will be present at a substantially higher concentration than any potentially cross sensitive substances, therefore this reaction is very selective.

Dräger claims the accuracy of the CO_2 0.1%/a tubes falls within a relative standard deviation of ±5 to 10%, over 68.3% of all measured readings, provided ambient operating conditions of 0° - 30°C (32° - 86°F) and a maximum absolute humidity of 30 mg H_2O/L (equating to approximately 99% relative humidity at 30°C) are not exceeded. For the CO_2 0.01%/a tubes, Dräger claims the relative standard deviation is ±10 to 15% (again, over 68.3% of all measured readings), with ambient operating conditions of 15° to 25°C (59° - 77°F) and a maximum absolute humidity of 23 mg H_2O/L (equating to approximately 99% relative humidity at 25°C). The type designation (0.1%/a or 0.01%/a) for these particular tubes indicates the lower end of the measuring range (0.1% and 0.01%) in Vol% while the letter indicates there has been no change made to the original construction of this tube. (Any improvements to the tube would result in a change to 0.1%/b, etc.)

Both the Dräger Accuro and Model 31 pumps are bellows type hand-held and actuated pumps that are used in conjunction with the Dräger tubes as the gas detection system. These pumps are designed to draw 100 ml (±5 ml) gas volume through the detector tube per stroke. While both the Dräger pumps were used in this test series, only the Model 31 is currently available in the Federal Stock System (stock number 6665-00-710-7815). Both the Dräger CO_2 0.1%/a gas detector tubes (stock number 6665-00-769-0945) and the 0.01%/a tubes (stock number 4220-01-006-1529), are also in the Federal Stock System.

Two important factors influence accuracy of the gas detector tubes: 1) flow rate of gas through the tube and 2) residence time

of the reactant with the reagent. Both of these parameters are influenced by the increased gas densities of hyperbaric environments. This test series evaluated the influence of those parameters on the accuracy of the gas detector system.

METHODS

This test series was conducted in four phases in accordance with NEDU Test Plan 94-21 (phases 1 through 3) and the Deep Dive '94 protocol (phase 4). During phase one, volumetric measurement of each pump was conducted to verify capacity. Phase two tested the pump/tube system at one atmosphere in order to verify specified tube accuracy. Phase three tested the accuracy of the pump/tube system under hyperbaric conditions at simulated depths of 9.1, 27.4, 45.7 and 50.3 meters of seawater (MSW) (30, 90, 150 and 165 feet of seawater (FSW)). Phase four tested the pump/tube system under saturation conditions to a maximum depth of 259 MSW (850 FSW).

The volumetric test series was conducted using a calibrated glass tube connected to the pump via nylaflow tubing through a rubber stopper on the top and vented on the side at the bottom to normal atmosphere. The bottom of the test set-up had a pliable liquid soap filled rubber bulb attached such that, after an initial coating of soap around the inside of the tube for lubrication, a soap film could be established across the diameter of the tube. The soap film was then displaced to a reference "zero" line. The pump was fully compressed and released and the level of rise of the soap film was read directly off the tube and recorded. A total of 20 test runs were conducted with four different pumps (2 each of the Model 31s and Accuros).

Phase two testing was conducted using six sources of certified CO_2 gas samples that would ultimately be used during phase three testing, plus two additional certified gas sources. All samples were collected in medical gas collection bags and sampled from the bag via an adaptor that provided an air-tight connection between the tube and the bag. The detector tubes used were Dräger Carbon Dioxide 0.1%/a tubes, which have two measuring ranges of 0.5 to 6.0 vol% (1 pump stroke, scale n=1) and 0.1 to 1.2 vol% (5 pump strokes, scale n=5). A total of 44 tests were conducted.

Phase three was conducted in the NEDU treatment chamber using U.S. Navy divers. The divers were instructed in the use of the pumps and tube pre-dive. Six certified CO_2 samples were randomly provided to the divers via gas collection bags filled on the surface prior to pressurization for each dive and coded so that the divers remained blind to the CO_2 concentration of the sample. As each diver tested a sample, the tube was also read from the surface through a chamber viewport and recorded. Only raw tube readings and sample bag numbers were recorded at this

point. Each diver sampled all six bags, three each with the Accuro pump and the Model 31 pump.

Phase four was conducted in the NEDU Ocean Simulation Facility (OSF) using eight U.S. Navy saturation divers. During the course of the dive, on a daily basis in conjunction with calibration of the installed Rosemount 880 CO_2 gas analyzers, a Dräger gas detector tube test of atmospheric CO_2 was conducted at a location adjacent to the installed gas analyzer sample port. Additionally, any time the OSF Atmospheric Analysis watch detected higher than normal CO_2 content in any OSF chamber, a test of the atmosphere was conducted using a Dräger CO_2 gas detector tube. During phase four, both 0.1%/a and 0.01%/a CO_2 gas detector tubes were used. The 0.01%/a tubes have a measuring range of 0.01% to 0.3 vol% (10 pump strokes, scale n=10).

During phases two and three, readings were rated as acceptable if they fell within ±10% of the known CO_2 concentration (Dräger's claimed relative standard deviation for the 0.1%/a detector tubes). During phase four, readings were rated as acceptable if they fell within ±10% (for the 0.1%/a detector tubes) or ±15% (for the 0.01%/a detector tubes) of the chamber CO_2 level as displayed on the electronic analyzer.

RESULTS

PHASE ONE

Phase one results are presented in Table 1. Results indicate that over the 20 separate test runs, all four pumps were well within manufacturer's volume specifications.

Table 1.

VOLUMETRIC TEST RESULTS

Model 31	Test	Results	Accuro	Test	Results
Pump #1.	1.	103 ml	Pump #1.	1.	98 ml
	2.	102 ml		2.	100 ml
	3.	102 ml		3.	99 ml
	4.	103 ml		4.	99 ml
Mean		102.5 ml			99 ml
Std Dev		0.50			0.7071
Pump #2.	1.	102 ml	Pump #2.	1.	100 ml
	2.	101 ml		2.	100 ml
	3.	101 ml		3.	99 ml
	4.	102 ml		4.	99 ml
Mean		101.5 ml			99.5 ml
Std Dev		0.50			0.50

PHASE TWO

Phase two results are presented in Appendix A. Pooling data from both pumps, 33 of 44 tests showed acceptable readings, which met or exceeded manufacturer's specifications for accuracy. However, the Accuro pumps resulted in significantly more acceptable readings (19 of 22) than did the Model 31 pumps (13 of 22) in spite of minimal differences between the measured volumes expelled by the pumps.

PHASE THREE

Phase three results are presented in Appendix B. Since the reagent conversion in the Dräger tube is proportional to the mass of the reacting gas (CO_2, in this case) all tube readings were corrected for depth and compared to the certified gas CO_2%. The error was taken as the fractional difference between the depth corrected tube reading and the actual CO_2 concentration. Based on Dräger's advertised accuracy for this particular type detector tube, a pass/fail criterion was established. For the Model 31 pumps, only 52% (12 of 23) were within the $\pm$ 10% margin of acceptability. For the Accuro pumps, 62.5% (15 of 24) were within the $\pm$10% margin of acceptability. Combining the Model 31 and Accuro pump results, the total acceptance rate at depth was 57% (27 of 47) [one data point was dropped due to acknowledged operator error].

PHASE FOUR

Detailed Phase four results are presented in Appendix C. Since metabolically produced CO_2 in a chamber is not influenced by depth, no tube corrections were required in this phase. While 105 samples were taken during the course of the dive, 33 tube samples had to be disregarded due to the fact that the range of the tube (0.01% - 0.3%) was exceeded and no follow up test was conducted at the time with the higher range tube. One of the 33 erroneous samples was disregarded due to the operator only compressing the pump 9 strokes instead of the required 10. Acceptance criteria for both tubes was based on the relative standard deviation for the individual tubes as advertised by Dräger. Based on these criteria and taking data from all depths, the results are summarized as follows:

Table 2.

<u>DEEP DIVE '94 TEST RESULTS</u>

	Model 31	Accuro	Overall
Acceptable	11 (30%)	7 (20%)	18 (25%)
Total Rdgs	37	35	72

DISCUSSION

Throughout the test series, it became obvious that a casual approach to the use of the Dräger gas detection system cannot be tolerated if maximum accuracy is to be achieved. The inherent systemic faults of the gas detector tube system have to be minimized in order to optimize results. These faults include operator influences such as incomplete pump compression, insufficient time allowed for pump expansion prior to reading the tube and, of course, differences between operators in reading the tubes. Proper maintenance of the pump and tubes will contribute to their optimum performance. Tubes should be stored at the proper temperature and then allowed to adjust to the sample gas temperature as much as possible prior to testing in order to avoid thermal stress of the reagent upon testing. Tubes exposed to high temperature can result in partial reagent evaporation which could cause weak coloring and/or longer stain length (since there would be less reagent to react with the CO_2) manifesting in erroneous readings. High humidity can contribute to erroneous high readings and very dry air can cause erroneous low readings. Observance of tube shelf life is critical.

Further, it became apparent during review of data from Phase four that the increased gas density common in saturation diving adversely affects flow rate of the gas through the tube and thereby lends itself to more frequent and increasingly unacceptable results. During Phase four, the vast majority of the acceptable readings (13 of 18) were obtained at less than 91.4 MSW (300 FSW).

The disparities in which model pump provided the most acceptable readings is felt to be most likely attributable primarily to operator influences.

CONCLUSIONS/RECOMMENDATIONS

The Dräger Co_2 gas detector tubes perform within the manufacturer's specification at one atmosphere. However, under hyperbaric conditions the Dräger tube can only provide a qualitative indicator of CO_2 within the chamber. Due to the Dräger tubes cost and limited utility, an alternate chamber CO_2 monitoring system should be considered.

NEDU recommends that Dräger tubes no longer be required as a back-up CO_2 monitoring system within a hyperbaric chamber. In case of a primary CO_2 monitor system failure in a saturation complex, a replacement CO_2 monitor should be immediately available. In the event of a power failure to the CO_2 monitor, the divers should use the built-in-breathing system until it is established that the atmosphere is safe to breath. For

recompression treatment chambers, the CO_2 can be controlled by ventilating the chamber according to the U.S. Navy Diving Manual.

OPERATIONAL GUIDELINES FOR USING DRÄGER TUBES

To achieve the most accurate results possible, it is imperative that the following guidelines be observed:

a) continuously observe the tube during measurement.

b) evaluate the indication immediately following the measurement.

c) use sufficient lighting.

d) use a light colored background for reading the tube.

e) compare the discoloration with an unused tube. Discoloration can present in any of three different situations:

(1) the color indication can end at a right angle to the tube's longitudinal axis. In this case, the concentration can be read directly against the scale.

(2) the color indication can be oblique (i.e. it runs in a slanting direction) to the tube's longitudinal axis such that there is a long and short side to the discoloration. In this case, the average reading between the long and short side then indicates the concentration.

(3) the end of the color indication becomes diffuse and indistinct. In this case, the final edge of the discoloration has to be read at the point where a faint discoloration is just visible.

Following these operational guidelines as well as ensuring proper storage conditions are met and shelf life has not been exceeded will maximize potential for accurate sampling results.

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2. Dräger-Tube Handbook (Drägerwerk AG, Lübeck, Germany,1994)

Surface Sample Testing

Sample %	Accuro Rdg	Difference	Acc/Rej	Model 31 Rdg	Difference	Acc/Rej
0.55 - N2	0.475	-0.14	Reject	0.55	0	Accept
	0.6	0.09	Accept	0.59	0.07	Accept
	0.5	-0.09	Accept			
1.01 - N2	1	0	Accept	0.7	-0.31	Reject
	1	0	Accept	1.25	0.24	Reject
	1	0	Accept	1.3	0.29	Reject
0.712-N2	0.65	-0.09	Accept	0.7	0	Accept
	0.7	0	Accept			
0.5 - He	0.45	-0.1	Accept	0.475	-0.05	Accept
	0.5	0	Accept			
	0.5	0	Accept			
.8153 - He	0.7	-0.14	Reject	0.75	-0.08	Accept
				1	0.23	Reject
				1	0.23	Reject
.252 - He	0.25	0	Accept	0.2	-0.21	Reject
	0.23	-0.09	Accept	0.3	0.19	Reject
				0.3	0.19	Reject
				0.4	0.59	Reject
2.51 - Air	2.1	-0.16	Reject	2.5	0	Accept
	2.45	-0.02	Accept	2.5	0	Accept
	2.25	-0.1	Accept	2.3	0.08	Accept
	2.5	0	Accept	2.5	0	Accept
.2000 - Air	0.2	0	Accept	0.2	0	Accept
	0.2	0	Accept	0.21	0.05	Accept
	0.2	0	Accept	0.2	0	Accept
	0.19	0.05	Accept	0.2	0	Accept

Draeger Tube Sampling at Depth

165 FSW, Depth Corr. = .1667
ATA = 6.0

Sample	Accuro	Corrected	Fractional Difference	Acc/Rej	Model 31	Corrected	Fractional Difference	Acc/Rej
.55 N2	4	0.66	0.21	Reject				
	3.5	0.583	0.06	Accept				
1.01 N2					6	1	-0.01	Accept
					5.5	0.916	-0.09	Accept
.712 N2	4.2	0.7	-0.02	Accept				
	3.5	0.583	-0.18	Reject				
.50 He					4	0.66	0.33	Reject
					3.1	0.516	0.03	Accept
.8153 He	4	0.66	-0.19	Reject				
	4.75	0.792	-0.03	Accept				
.252 He					2.1	0.35	0.39	Reject
					1.8	0.3	0.19	Reject
Mean			-0.025				0.14	
Std Dev			0.14				0.18	

150 FSW, Depth Corr. = .1803
ATA = 5.5454

Sample	Accuro	Corrected	Fractional Difference	Acc/Rej	Model 31	Corrected	Fractional Difference	Acc/Rej
.55 N2	3	0.54	-0.02	Accept	2.5	0.45	-0.18	Reject
1.01 N2	5.5	0.99	-0.02	Accept	6	1.08	0.07	Accept
.712 N2	4.1	0.739	0.04	Accept	4	0.721	0.01	Accept
.50 He	3.2	0.57	0.15	Reject	2.75	0.495	-0.01	Accept
.8153 He	4.75	0.856	0.05	Accept	4.5	0.811	0.01	Accept
.252 He	1.9	0.342	0.36	Reject	1.8	0.324	0.29	Reject
Mean			0.09				0.03	
Std Dev			0.13				0.14	

Draeger Tube Sampling at Depth

90 FSW, Depth Corr. = .2682
ATA = 3.7272

Sample	Accuro	Corrected	Fractional Difference	Acc/Rej	Model 31	Corrected	Fractional Difference	Acc/Rej
.55 N2	1.8	0.483	-0.12	Reject	2	0.536	0.03	Accept
1.01 N2	3.1	0.831	-0.18	Reject	3	0.805	-0.2	Reject
.712 N2	2.75	0.737	0.04	Accept	2.2	0.59	-0.17	Reject
.50 He	1.8	0.483	-0.03	Accept	2.2	0.59	0.18	Reject
.8153 He	2	0.536	-0.34	Reject	3	0.805	-0.01	Accept
.252 He	1	0.268	0.06	Accept	2	0.536	1.13	Dropped
Mean			-0.095				0.16	
Std Dev			0.14				0.14	

30 FSW, Depth Corr. = . 5238
ATA = 1.9091

Sample	Accuro	Corrected	Fractional Difference	Acc/Rej	Model 31	Corrected	Fractional Difference	Acc/Rej
.55 N2	1.2	0.628	0.14	Reject	1.4	0.733	0.33	Reject
1.01 N2	1.8	0.942	-0.07	Accept	2	1.047	0.04	Accept
.712 N2	1.5	0.786	0.1	Accept	1.5	0.786	0.1	Accept
.50 He	1	0.524	0.05	Accept	1.4	0.733	0.47	Reject
.8153 He	1.5	0.786	-0.04	Accept	1.5	0.786	-0.04	Accept
.252 He	0.5	0.262	0.04	Accept	0.6	0.314	0.25	Reject
Mean			0.04				0.19	
Std Dev			0.07				0.18	

DEEP DIVE '94 DATA

Depth	Analyzer	Tube	% Delta	Acc/Rej
101-103				
0.30%	0.234	0.30	28.21	R
	0.233	0.30	28.76	R
	0.233	0.30	28.76	R
	0.231	0.30	29.87	R
*	0.234	0.25	6.84	A
*	0.234	0.20	-14.53	A
*	0.233	0.24	3	A
*	0.233	0.20	-14.16	A
*	0.231	0.23	-0.43	A
	0.234	0.26	11.11	A
175-178	1 Bad (N=9 vs 10)			
0.30%	0.20	0.26	30	R
	0.20	0.30	50	R
	0.20	0.25	25	R
	0.20	0.30	50	R
	0.20	0.30	50	R
*	0.20	0.25	25	R
*	0.20	0.26	30	R
*	0.20	0.23	15	A
*	0.20	0.22	10	A
196-200				
6.00%	0.20	0.40	100	R
	0.20	0.40	100	R
	0.20	0.25	25	R
*	0.20	0.30	50	R
*	0.20	0.50	150	R
*	0.20	0.40	100	R
*	0.20	0.40	100	R
*	0.20	0.30	50	R
	0.29	0.50	72.41	R
*	0.29	0.50	72.41	R
	0.20	0.20	0	A
	0.20	0.20	0	A
0.30%	0.29	0.30	3.45	A
*	0.29	0.30	3.45	A
288-295	10 Bad (Off scale - 0.3%)			
0.30%	0.29	0.02	-93.1	R
*	0.29	0.30	3.45	A
391-	10 Bad (Off scale - 0.3%)			

Depth	Analyzer	Tube	% Delta	Acc/Rej
400-				
6.00%	0.33	0.45	36.36	R
*	0.33	0.45	36.36	R
0.30%	0.33	0.30	-9.09	A
488-493				
6.00%*	0.19	0.30	57.89	R
0.30%*	0.176	0.30	70.45	R
*	0.177	0.30	69.49	R
*	0.177	0.30	69.49	R
*	0.177	0.25	41.24	R
*	0.177	0.25	41.24	R
	0.176	0.30	70.45	R
	0.176	0.30	70.45	R
	0.177	0.30	69.49	R
	0.177	0.25	41.24	R
	0.177	0.30	69.49	R
	0.19	0.30	57.89	R
*	0.19	0.15	-21.05	R
575-578	4 Bad (Off scale - 0.3)			
0.30%	0.181	0.30	65.75	R
*	0.181	0.30	65.75	R
*	0.181	0.30	65.75	R
*	0.181	0.30	65.75	R
*	0.181	0.30	65.75	R
*	0.181	0.28	54.7	R
650-				
0.30%	0.31	0.30	-3.23	A
*	0.31	0.30	-3.23	A
701-	2 Bad (Off scale - 0.3)			
6.00%	0.24	0.55	129.17	R
768-				
0.30%*	0.12	0.25	108.33	R
	0.12	0.25	108.33	R
850-	6 Bad (Offscale - 0.3)			
6.00%	0.355	0.95	167.61	R
*	0.355	0.95	167.61	R
*	0.243	0.50	105.76	R
	0.243	0.50	105.76	R
*	0.235	0.60	155.32	R
	0.235	0.60	155.32	R
0.30%	0.17	0.30	76.47	R
*	0.17	0.30	76.47	R
	0.26	0.30	15.38	A
*	0.26	0.30	15.38	A

* Indicates Model 31 pump used to sample
33 samples went out of range (Bad)
6.0% Tubes = ±10% rel std dev
0.3% Tubes = ±15% rel std dev